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A Reversible Single-Crystal to Single-Crystal Thermal Phase Transformation of 3-(2-Bromo-4-(1-methylethyl)phenyl)-1,1-dimethyl urea

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Abstract: 3-(2-Bromo-4-(1-methylethyl)phenyl)-1,1-dimethylurea was synthesized and structurally characterized at 296 K, 200 K and 140 K. A reversible thermal phase transformation was observed at ~170–180 K. On cooling, the structure transforms from a monoclinic to a triclinic crystal system. The isopropyl group is disordered above the phase transition temperature but is ordered below the transition temperature.

Keywords: crystal-to-crystal; 1,1-dimethylurea; reversible; phase transition; thermal

1. Introduction

Urea-containing compounds are established as precursors for several biologically active agents [1–4]. Various efficient procedures have been used for the synthesis of ureas [5–14]. The most recent examples involve reactions of primary amines with *S*,*S*-dimethyl dithiocarbonate in water followed by reactions with secondary amines [15]; reactions of aromatic amines with secondary amines in the presence of carbon monoxide, sulfur and oxygen in dimethylformamide [16]; and reactions of benzylamine with secondary amines in the presence of a ruthenium catalyst [17]. Other synthetic methods involve the catalytic reaction of carboxylic acids with hydroxylamine hydrochloride followed by reaction with primary amines [18]; conversion of aryl chlorides to the corresponding isocyanates using a palladium catalyst followed by reaction with secondary amines [19]; and conversion of isonitriles to the corresponding isocyanates using dimethyl sulfoxide followed by reaction with *tert*-butylamine [20]. The reaction of aromatic ureas with a lithium reagent followed by electrophiles is one of the most common methods used to produce substituted derivatives [21–25].

Polymorphic phase transformation is an area of continued research interest [26–35]. The transformation process is an indication of the fine balance in the interactions within the crystal that can be tipped by a relatively small change in conditions [36,37]. In most cases, such transformations proceed with loss of single-crystal integrity, such that a single crystal of the starting solid phase transforms into a polycrystalline sample of the product. Where the structural reorganization involved is small, transformation of a single crystal of the starting material may produce a single crystal of the product phase. Additionally, the process may be reversible but this is rare in organic crystals [30–35]. Enantiotropic behavior has been observed unsurprisingly between forms with very similar unit cell parameters [31,32], but transformation more commonly involves larger shifts in the parameters [33–35]. Polymorphism and polymorphic phase transformations are difficult to predict and are often discovered fortuitously [26].

In the current paper, we investigated the synthesis, characterization and reversible single-crystal to single-crystal thermal phase transformation of 3-(2-bromo-4-(1-methylethyl)phenyl)-1,1-dimethylurea.

2. Results and Discussion

Phase transformation: In the process of characterization of 3-(2-bromo-4-(1-methylethyl)phenyl) -1,1-dimethylurea following synthesis, the crystal structure was determined initially at 296 K. The structure, $\mathbf{1_{HT}}$ (Table 1), is monoclinic, $P2_1/c$ (with unit cell parameters a = 12.117(2) Å, b = 10.0335(10) Å, c = 12.816(2) Å, β = 117.82(2)°, volume = 1377.9(5) Å^3). Data collection performed at 140 K in an attempt to improve the quality of the refined structure revealed a different structure (**2**), indicating that a phase transition had occurred on cooling. Structure **2** is triclinic, $P\bar{1}$, with unit cell parameters a = 11.8916(7) Å, b = 9.9293(6) Å, c = 12.4631(7) Å, α = 92.720(5)°, β = 116.190(5)°, γ = 81.000(5)°, volume = 1303.86(14) Å^3. (This unit cell has been used for ease of comparison with the monoclinic structure **1**. The reduced cell is 9.9290(6) Å, 11.8920(7) Å, 12.4630(7) Å, 63.810(5)°, 87.280(5)°, 81.000(5)°). The matrix for the transformation from **2** to **1** is (1.0072, −0.189, −0.0073, 0, 1.0088, 0, −0.0149, 0.063, 1.0164).

Table 1. Experimental and structure refinement data.

Identification Code	$\mathbf{1_{HT}}$	$\mathbf{1_{LT}}$	**2**
Empirical formula	$C_{12}H_{17}BrN_2O$	$C_{12}H_{17}BrN_2O$	$C_{12}H_{17}BrN_2O$
Formula weight	285.18	285.18	285.18
Temperature (K)	296(2)	200(2)	140(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	12.117(2)	11.8696(12)	11.8916
b (Å)	10.0335(10)	10.0171(7)	9.9293(6)
c (Å)	12.816(2)	12.7306(12)	12.4631(7)
α (°)	90	90	92.720(5)
β (°)	117.82(2)	117.199(13)	116.190(5)
γ (°)	90	90	81.000(5)
Volume (Å^3)	1377.9(5)	1346.3(3)	1303.86(14)
Z	4	4	4
σ_{cal} (Mg/m^3)	1.375	1.407	1.453
μ (mm^{-1})	2.967	3.037	3.135
F(000)	584	584	584
Crystal size (mm^3)	0.272 × 0.177 × 0.122	0.309 × 0.170 × 0.106	0.301 × 0.209 × 0.099
Reflections collected	4752	7310	11649
Independent reflections	2718	3229	11030
R(int)	0.0622	0.0284	0.0751
Data/restraints/parameters	2718/109/166	3229/110/170	11,649/0/297
Goodness-of-fit on F^2	0.813	1.036	0.913
$R1[I > 2\sigma(I)]$	0.0614	0.0673	0.0446
wR2	0.1619	0.1644	0.1029
$R1$ (all data)	0.1744	0.1117	0.0850
wR2	0.1827	0.1961	0.1081

The transformation occurs in a single-crystal to single-crystal manner, so it was possible to determine the unit cell parameters as a function of temperature. A plot of the cell parameters recorded for a single crystal shows a discontinuity in the 170–180 K temperature range (Figure 1). Notably, the transformation occurs reversibly. Thus, the monoclinic structure ($\mathbf{1_{LT}}$) discussed below was determined after cooling a crystal past the transition temperature to 150 K, before warming it again to 200 K.

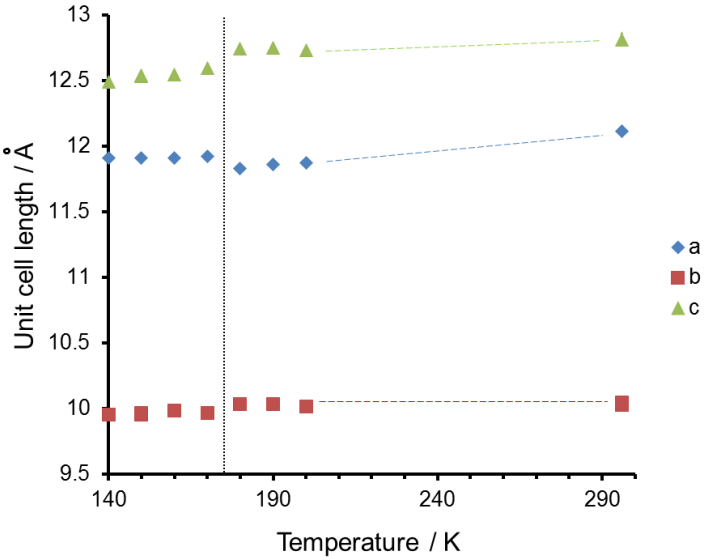

Figure 1. A plot of the unit cell parameters as a function of temperature. The dotted vertical line indicates the phase transition point.

Monoclinic structure: The asymmetric unit of $\mathbf{1_{LT}}$ consists of one molecule of 3-(2-bromo-4-(1-methylethyl)phenyl)-1,1-dimethylurea (Figure 2a). In the molecule, the angle between the planes through the bromophenyl and dimethylurea groups is 59.24(16)°. The isopropyl group is disordered with refined occupancies of 0.725(16) and 0.275(16) for the two components. The most acute torsion angles for the isopropyl group are C5–C4–C7–C9 = −46.3(11)° and C3–C4–C7A–C8A = −61.6(11)° for the major and minor components, respectively. In the structure (Figure 2b), chains of molecules are formed along [010] by N–H···O hydrogen bonds (with the geometry N1–H1···O1 = 143.8°, N1···O1 = 2.869(4) Å).

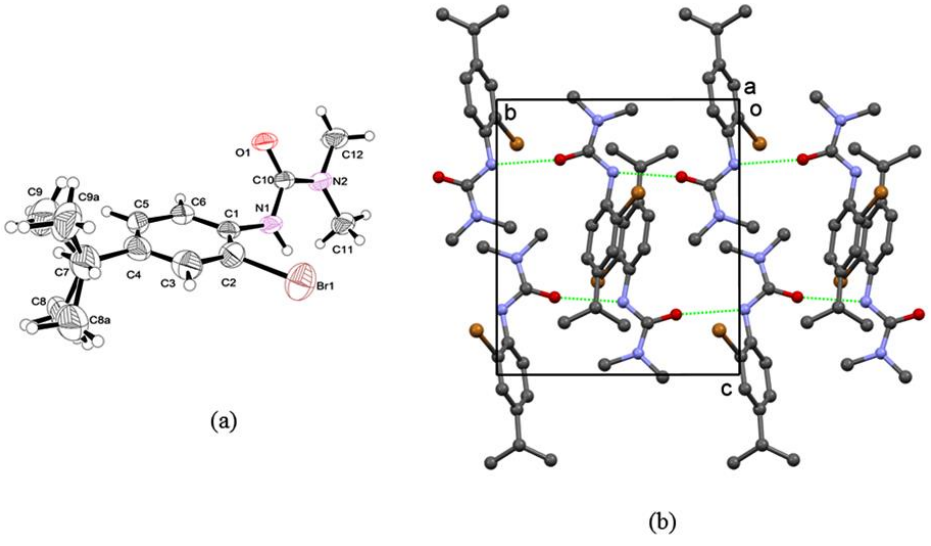

Figure 2. (**a**) An ortep representation of the asymmetric unit of $\mathbf{1_{LT}}$ showing the disordered isopropyl group; (**b**) Crystal packing viewed down the *a* axis with hydrogen atoms and one disorder component omitted for clarity. Hydrogen bonds are shown as dashed lines.

Triclinic structure: Structure **2** has two independent molecules in the asymmetric unit (Figure 3a). The angles between the planes through the bromobenzene and dimethylurea groups are 69.25(9)° and 49.51(11)° for the two molecules. It is notable that the average of these values for the interplanar angles

is the same as that for the single independent molecule in $\mathbf{1_{LT}}$. Unlike in $\mathbf{1_{LT}}$, the isopropyl groups are ordered in **2**, and the most acute torsion angles are C3–C4–C7–C8 = 51.9(5)° and C17–C16–C19–C20 = −28.6(5)°. In the structure (Figure 3b), chains of N–H…O hydrogen-bonded molecules are formed along [010].

The two molecules alternate along the chain leading to the formation of two hydrogen bonding interactions (with the geometries N1–H1…O2 = 149.8°, N1…O2 = 2.872(4) Å and N3–H3A…O1 = 134.5°, N3…O1 = 2.799(4) Å). Although not identical, the chains of the hydrogen-bonded molecules are similar in both **1** and **2** as indicated by the overlay plot in Figure 4.

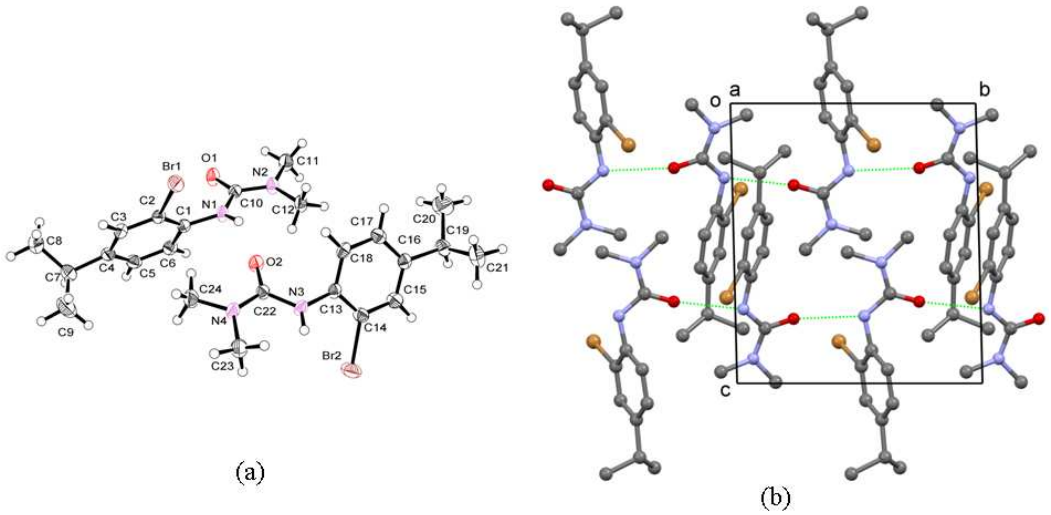

Figure 3. (**a**) An ortep representation of the asymmetric unit of **2** showing the two molecules in the asymmetric unit; (**b**) Crystal packing viewed down the *a* axis with the hydrogen atoms omitted for clarity. Hydrogen bonds are shown as dashed lines.

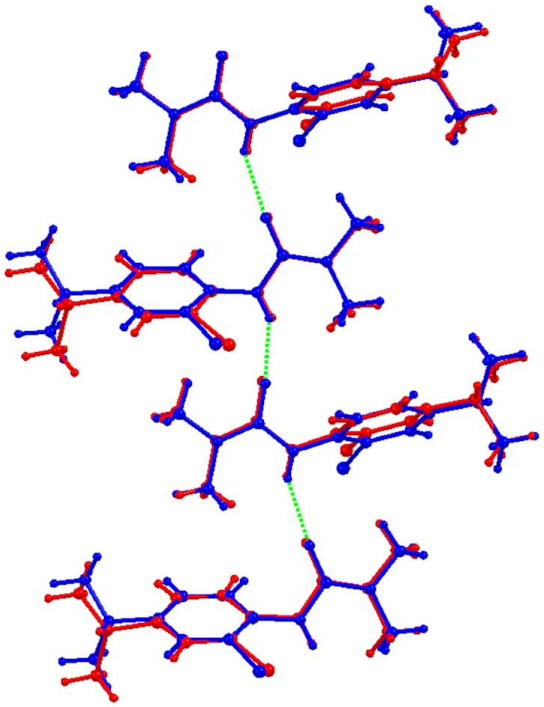

Figure 4. An overlay of the hydrogen bonded chains from $\mathbf{1_{LT}}$ (red) and **2** (blue). The minor disorder component in **1** has been omitted for clarity.

On cooling the crystal from 296 K, the structure transforms from a monoclinic to a triclinic crystal system, retaining a similar unit cell volume. The single molecule in the asymmetric unit of the monoclinic structure above the phase transition temperature has a disordered isopropyl group. The refined ratios of the disordered components of the isopropyl group at 296 K and 200 K are 0.645(15)/0.355(15) and 0.725(16)/0.275(16), respectively. The values are significantly different from the 1:1 ratio of the two conformations of the independent molecules observed in the ordered structure of **2**. This suggests that the isopropyl group has some rotational freedom about the C-C(CH_3)$_2$ bond. Disorder in isopropyl groups is common, but significant isopropyl rotation is expected to occur only in exceptional circumstances as, for example, observed in 1-(benzoyl)-3-((5′-isopropyl-2′-methylphenoxy)acetamino) thiourea [30].

3. Experimental Section

3.1. General

Melting point determination was performed on a Gallenkamp melting point apparatus. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AV400 spectrometer. The chemical ionization (ammonia) mass spectrum was recorded on a Quattro II spectrometer at 50 eV. Accurate mass data were recorded on a MAT900 instrument.

3.2. Synthesis of 3-(2-Bromo-4-(1-methylethyl)phenyl)-1,1-dimethylurea

The title compound was produced from reaction of 2-bromo-4-(1-methylethyl)aniline (10 mmol) and dimethylcarbamoyl chloride (11 mmol) in dichloromethane (40 mL) under reflux for 1 h in the presence of excess triethylamine (15 mmol). On cooling, the solvent was removed under reduced pressure and the residue obtained was purified by crystallization from diethyl ether to give the title compound as colourless crystals. Mp 93–94 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 7.3 Hz, 1 H, H-6), 7.33 (s, 1 H, H-3), 7.15 (d, *J* = 7.3 Hz, 1 H, H-5), 6.91 (br s, exch., 1 H, NH), 3.06 (s, 6 H, N(CH_3)$_2$), 2.83 (septet, *J* = 7.2 Hz, 1 H, CH), 1.20 (d, *J* = 7.2 Hz, 6 H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.1 (s, C=O), 135.2 (s, C-4), 133.3 (s, C-1), 131.3 (d, C-3), 125.0 (d, C-5), 123.9 (s, C-6), 121.4 (d, C-2), 35.1 (q, N(CH_3)$_2$), 31.8 (d, CH); 24.0 (q, CH(CH_3)$_2$). EI-MS: *m/z* (%) 284 (M^+, 5), 177 (11), 72 (100); CI-MS: *m/z* (%) 302 ([M + NH_4]$^+$, 2), 285 (MH^+, 100), 177 (22), 72 (100). HRMS (CI): calculated for $C_{12}H_{17}BrN_2O$ (MH^+): 285.0603; found: 285.0603. IR (KBr) ν_{max} 3292, 2990, 2496, 1690, 1580, 1520, 1480 cm^{-1}. Anal. Calcd for $C_{12}H_{17}BrN_2O$: C, 50.54; H, 5.96; N, 9.82. Found: C, 50.34; H, 5.83; N, 9.97%.

3.3. Structure Determination

Single-crystal XRD data were collected on an Agilent SuperNova Dual Atlas diffractometer with a mirror monochromator [Mo (λ = 0.7107 Å)] equipped with a Cryosystems cooling apparatus. The crystal structures were solved and refined using SHELX [38]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined using a riding model. Methyl C–H bonds were fixed at 0.98 A, with displacement parameters 1.5 times Ueq(C), and were allowed to spin about the C–C bond. Aromatic C-H distances were set to 0.95 A and their U(iso) set to 1.2 times the Ueq for the atoms to which they are bonded. The disordered isopropyl group in **1** was refined with two components and restrained geometry. Crystal data, data collection and structure refinement details are summarized in Table 1. CCDC 1532132-1532134 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

4. Conclusions

3-(2-Bromo-4-(1-methylethyl)phenyl)-1,1-dimethylurea was synthesized and its structure was established at 296 K, 200 K and 140 K. A phase transformation was observed at ~170–180 K on cooling

the crystal. The structure transforms from a monoclinic to a triclinic crystal system in a single-crystal to single-crystal manner, retaining a similar unit cell volume. The transformation is reversible on warming. The isopropyl group is disordered above the phase transition temperature but is ordered below the transition temperature.

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Author Contributions: Gamal A. El-Hiti performed the synthesis of the title compound and established its structure by NMR, mass spectroscopy and analytical data. Benson M. Kariuki carried out the X-ray structure determination and thermal phase transformation of the title compound. Both authors wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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